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# **Electrochemical Determination of Thermodynamic Properties of Manganese Sulfate and Cadmium Oxysulfate**

By Seth C. Schaefer



UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8809

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**BUREAU OF MINES**

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# UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	angstrom	kcal	kilocalorie
atm	atmosphere	kcal/mol	kilocalorie per mol
cal/mol·K	calorie per mole, per degree kelvin	min	minute
cal/mv	calorie per millivolt	mv	millivolt
h	hour	wt pct	weight percent
K	kelvin		

# ELECTROCHEMICAL DETERMINATION OF THERMODYNAMIC PROPERTIES OF MANGANESE SULFATE AND CADMIUM OXYSULFATE

By Seth C. Schaefer<sup>1</sup>

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## ABSTRACT

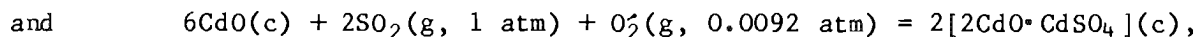
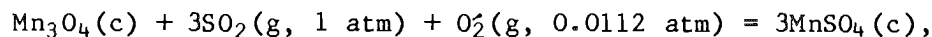
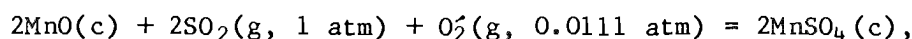
The Bureau of Mines investigated thermodynamic properties of  $\text{MnSO}_4$  and  $2\text{CdO} \cdot \text{CdSO}_4$  to obtain basic thermodynamic data applicable to the treatment of mineral concentrates during roasting and sintering processes. Standard Gibbs energies of formation were determined with high-temperature galvanic cells using stabilized  $\text{ZrO}_2$  as the electrolyte. Potential measurements were obtained from the cells

$\text{Pt}, \text{MnSO}_4, \text{MnO}, \text{SO}_2(\text{g}, 1 \text{ atm}) // \text{ZrO}_2 // \text{O}_2^*(\text{g}, 0.0111 \text{ atm}), \text{Pt},$

$\text{Pt}, \text{MnSO}_4, \text{Mn}_3\text{O}_4, \text{SO}_2(\text{g}, 1 \text{ atm}) // \text{ZrO}_2 // \text{O}_2^*(\text{g}, 0.0112 \text{ atm}), \text{Pt},$

and  $\text{Pt}, 2\text{CdO} \cdot \text{CdSO}_4, \text{CdO}, \text{SO}_2(\text{g}, 1 \text{ atm}) // \text{ZrO}_2 // \text{O}_2^*(\text{g}, 0.0092 \text{ atm}), \text{Pt}.$

The overall cell reactions are, respectively,



where  $\text{O}_2^*$  refers to the indicated partial pressure of oxygen at the reference electrode.

Equilibrium oxygen pressures for the Mn-S-O system were measured and may be expressed as

$$\log p_{\text{O}_2} = - \frac{35,848}{T} + 24.67 \quad (896.5-946.3 \text{ K}),$$

$$\log p_{\text{O}_2} = - \frac{46,973}{T} + 36.26 \quad (971.2-1,104.1 \text{ K}),$$

and  $\log p_{\text{O}_2} = - \frac{44,020}{T} + 33.63 \quad (1,128.6-1,226.8 \text{ K}),$

where  $p_{\text{O}_2}$  is the equilibrium oxygen pressure in atmospheres and the temperature (T) is in kelvins. An invariant point was determined at 960 K for the Mn-S-O system, and a phase transition of  $\text{MnSO}_4$  was detected at 1,123 K. Similarly, equilibrium oxygen pressures for the Cd-S-O system may be expressed as

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$$\log p_{O_2} = - \frac{39,231}{T} + 27.61 \quad (1,036.8-1,208.2 \text{ K}).$$

Standard Gibbs energies of formation of  $MnSO_4$  and  $2CdO \cdot CdSO_4$  were derived from these measurements and auxiliary data from the literature and may be expressed as follows:

$$\Delta G_f^\circ(MnSO_4) = -260.609 + 91.41 \times 10^{-3}T \pm 0.169 \text{ kcal/mol} \quad (896.5-946.3 \text{ K}),$$

$$\Delta G_f^\circ(MnSO_4) = -267.958 + 99.25 \times 10^{-3}T \pm 0.176 \text{ kcal/mol} \quad (971.2-1,123 \text{ K}),$$

$$\Delta G_f^\circ(MnSO_4) = -262.884 + 94.73 \times 10^{-3}T \pm 0.202 \text{ kcal/mol} \quad (1,123-1,226.8 \text{ K}),$$

$$\text{and } \Delta G_f^\circ(2CdO \cdot CdSO_4) = -433.260 + 222.25 \times 10^{-3}T \pm 0.610 \text{ kcal/mol} \\ (1,036.8-1,208.2 \text{ K}).$$

The standard enthalpy of formation of  $MnSO_4$ , derived by the third-law method is

$$\Delta H_f^{298} = -257.674 \pm 0.20 \text{ kcal/mol}.$$

## INTRODUCTION

Metal sulfates and basic or oxysulfates occur in nature or may be formed when concentrates are treated in unit operations such as roasting and sintering. Selective sulfation has become an important metallurgical process, owing in large part to the availability of the fluid-bed reactor, which permits close control of temperature and gas composition. A scientific approach to sulfation chemistry requires thermodynamic data of sulfation reactions in simple and complex systems.

As a part of its program to expand the base of scientific information required to develop innovative technologies, the Bureau of Mines investigated thermodynamic properties of  $MnSO_4$  (manganese sulfate) and  $2CdO \cdot CdO_4$  (cadmium oxysulfate). These data were developed for application in research efforts to maximize recovery of important metals, with minimal energy requirements. The only cadmium mineral of any importance is greenockite,  $CdS$ , usually associated with sphalerite in trace amounts. Cadmium is recovered as a by-product in zinc and lead smelting and is used primarily in production of alloys with low melting points. Manganese is an important alloying element in steel production. Since the United States produces only a small percentage of its manganese requirements, a great deal of attention has been given to effective utilization of manganese and improved recovery from its ores. A compilation (11)<sup>2</sup> of sulfation equilibria shows a need for further study by modern techniques to obtain thermodynamic data for  $MnSO_4$ , and  $2Cd \cdot CdSO_4$ , as well as for  $CdSO_4$ ,  $FeSO_4$ , and  $MgSO_4$ .

The most commonly used method for determining sulfation equilibria is the measurement of total decomposition pressure within a closed system. However, desorption of moisture from incompletely dried samples causes high pressure readings that result in significant error when the total pressure is small. This method is also subject to slight errors from thermal segregation of the gas species (8, 27). A second method (12, 27) used to study sulfation equilibria is decomposition of the

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<sup>2</sup>Underlined numbers in parentheses refer to items in the list of references at the end of this report.

sulfate sample in the presence of substances that fix the oxygen pressure. In this case, the total pressure is no longer subject to error from thermal segregation, and the range of total pressure is adjusted by choice of a metal-metal oxide couple that controls the oxygen pressure over the sulfate. A variety of flow methods (3, 25), which employ a moving gas stream to fix the oxygen pressure, have also been used to study sulfate reactions, but difficulties in achieving equilibrium gas composition at the reaction site often yield erroneous results. Differential thermal analyses studies (11) provide qualitative data to detect the onset of reactions in a sulfate sample heated at a constant rate in a stream of  $\text{SO}_2$  and  $\text{O}_2$ . Calorimetric methods have also been used (1, 23-24) to obtain standard-state data for sulfates and oxysulfates of stoichiometric composition. Prediction of chemical behavior by means of calorimetric data can be seriously in error because the properties of the hypothetical standard state may be quite different from the properties that exist in actual equilibrium conditions for complex systems at high temperatures. Recently, electromotive force (emf) techniques using a stabilized  $\text{ZrO}_2$  (zirconia) electrolyte were used to investigate metal oxide-metal sulfate equilibria (4-5, 17, 20, 28). The emf method used by the Bureau was specifically designed to obtain accurate equilibrium oxygen dissociation pressures of metal oxide-metal sulfate or metal oxide-metal oxysulfate systems. This technique permits direct determination of the thermodynamic stability of these complex systems and Gibbs energies of formation of sulfates and oxysulfates from their oxides at elevated temperatures.

Application of stabilized  $\text{ZrO}_2$  as a selective solid-anion electrolyte has been demonstrated in determining Gibbs energies for cell reactions involving metal-metal oxide systems at elevated temperatures (13). Within the limitation of the ionic domain of stabilized  $\text{ZrO}_2$  (22), any equilibrium involving oxygen may be investigated by this technique. The method is based on the measurement of the difference in chemical potential between a reference electrode of known oxygen potential and the oxygen potential of the electrode to be determined. In this investigation, the difference was measured between the oxygen potential of a reference electrode containing a certified standard of  $\text{O}_2$  in nitrogen, and the oxygen potential of an electrode consisting of a mixture of a metal oxide and its coexisting sulfate or a metal oxide and its coexisting oxysulfate. The standard states are the saturated coexisting phases. The transport number of oxygen is essentially unity in the range of oxygen potential of this investigation (22). The relationship between the open-circuit potential of the cell and the Gibbs energy change for the actual cell reaction is

$$\Delta G(\text{reaction}) = -nFE, \quad (1)$$

where  $\Delta G$  is the change in Gibbs energy for the cell reaction,  $n$  is the number of electrochemical equivalents in the reaction,  $F$  is the Faraday constant (23.061 cal/mv equivalent), and  $E$  is the emf in millivolts.

## EXPERIMENTAL WORK

### Materials

High-purity reagents were obtained from commercial sources and used without further purification. Analyses of these reagents were confirmed, and the results are presented in table 1. Anhydrous-grade  $\text{SO}_2$  and a certified standard mixture of  $\text{O}_2$  in nitrogen were used. Actual analyses for  $\text{O}_2$  in  $\text{O}_2$ -nitrogen mixtures were checked by the emf method. The  $\text{O}_2$ -nitrogen mixture was dried by passing through  $\text{Mg}(\text{ClO}_4)_2$  (magnesium perchlorate), and the  $\text{SO}_2$  was dried by passing through a column packed with  $\text{CaSO}_4$  (calcium sulfate).



TABLE 1. - Impurities detected in reagents

Reagent and impurity elements <sup>1</sup>	wt pct	Reagent and impurity elements <sup>1</sup>	wt pct
MnO:		MnSO <sub>4</sub> :	
Aluminum.....	<0.003	Magnesium.....	<0.001
Magnesium.....	<.03	Nickel.....	<.03
Silicon.....	<.01	Silicon.....	<.01
Mn <sub>3</sub> O <sub>4</sub> :		Silver.....	<.003
Aluminum.....	.07	CdO:	
Copper.....	<.001	Sodium.....	<.1
Iron.....	.13	CdSO <sub>4</sub> :	
Magnesium.....	.07	Impurities.....	ND
Nickel.....	.06		
Sodium.....	.12		

ND No impurities detected.

<sup>1</sup>Impurities not detected by spectrochemical analyses except as noted in the table were Ag, Al, As, B, Ba, Be, Bi, Ca, Cb, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hf, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Sb, Si, Ta, Ti, V, W, Y, Zn, and Zr.

NOTE.--X-ray emission and chemical analyses were performed by R. F. Farrell, a research chemist for the analytical laboratory at the Albany Research Center, Bureau of Mines, Albany, OR.

nitrogen were used. Actual analyses for O<sub>2</sub> in O<sub>2</sub>-nitrogen mixtures were checked by the emf method. The O<sub>2</sub>-nitrogen mixture was dried by passing through Mg(ClO<sub>4</sub>)<sub>2</sub> (magnesium perchlorate), and the SO<sub>2</sub> was dried by passing through a column packed with CaSO<sub>4</sub> (calcium sulfate).

#### Apparatus and Procedure

Internal arrangement of the cell components is illustrated in figure 1.<sup>3</sup> The apparatus, potentiometer, and standardized thermocouple have been described in previous publications (18-19). The reference electrode was a certified standard mixture of O<sub>2</sub> in nitrogen, and the electrode of unknown oxygen potential consisted of a 1:1 molar mixture of MnO plus MnSO<sub>4</sub>, a 1:1 molar mixture of Mn<sub>3</sub>O<sub>4</sub> plus MnSO<sub>4</sub>, or a 1:1 mixture of CdO plus 2CdO·CdSO<sub>4</sub>. Measurements were completed in 2 days, following a 12-h stabilization period at 1,040 K. Emf measurements were made with a Keithley model 642 high-input impedance digital electrometer. Reversibility of the cell reaction was checked by approaching equilibrium from above and below a specified temperature. Cell response to temperature change was rapid above 1,000 K, and potentials stabilized within 1 h after a steady-state temperature was reached. Experiments were repeated two or three times for each cell before the cell was dismantled and the electrode removed for X-ray analyses. Reproducibility was checked by obtaining measurements of several separate cells for each determination.

<sup>3</sup>Reference in the figures or text to specific trade names does not imply endorsement by the Bureau of Mines.

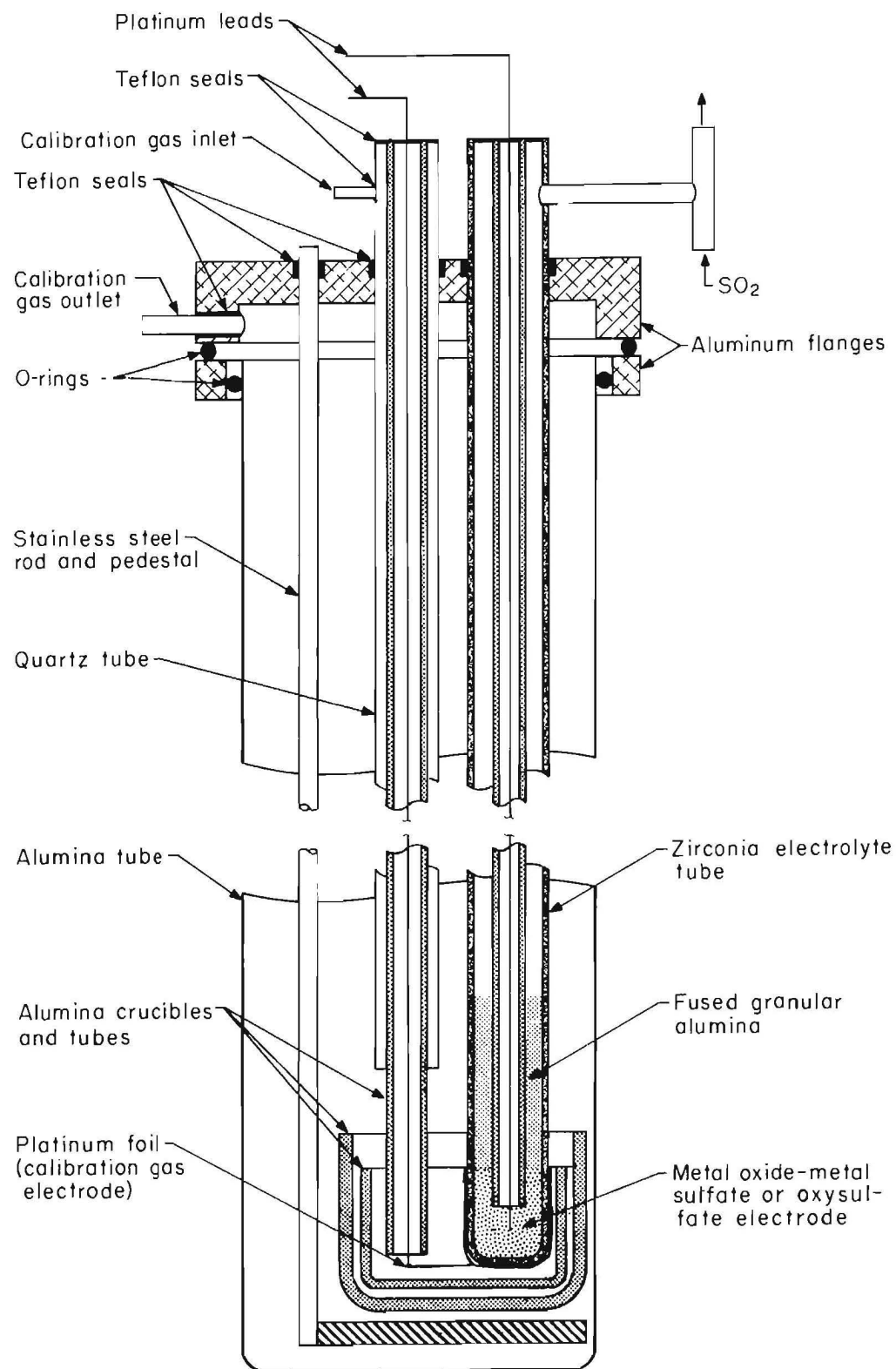
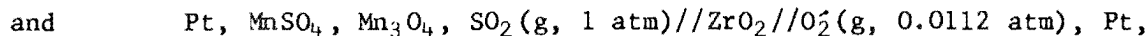
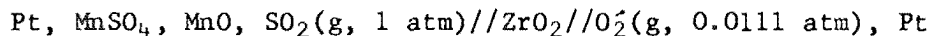


FIGURE 1. - High-temperature galvanic cell.

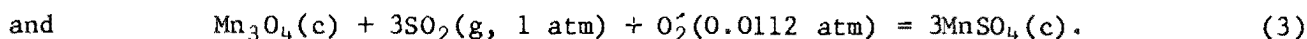
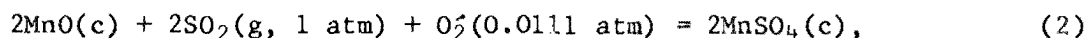
## RESULTS AND DISCUSSION

MnSO<sub>4</sub>

The equilibrium oxygen pressures and corresponding Gibbs energy changes for the MnO-MnSO<sub>4</sub>-SO<sub>2</sub>-O<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub>-MnSO<sub>4</sub>-SO<sub>2</sub>-O<sub>2</sub> systems were determined by measuring the potentials of the reversible cells



where the O<sub>2</sub><sup>\*</sup> refers to the indicated partial pressure of oxygen at the respective reference electrodes. The overall cell reactions are as follows:



Potential measurements from the two types of cells that were used for the MnSO<sub>4</sub> determination are given in table 2. These results may be expressed as a function of temperature by the least squares equations and standard error of estimate as follows:

$$E = 1,778.15908 - 1.32084T \pm 1.32 \quad (896.5-946.3 \text{ K for reaction 2}), \quad (4)$$

$$E = 2,330.01553 - 1.89540T \pm 2.45 \quad (971.2-1,104.1 \text{ K for reaction 3}), \quad (5)$$

and  $E = 2,183.52496 - 1.76486T \pm 4.03 \quad (1,128.6-1,226.8 \text{ K for reaction 3}), \quad (6)$

where E is expressed in millivolts. Smooth emf data from equations 4, 5, and 6 are given in columns 4 and 8 of table 2. Representative emf-versus-temperature data for reactions 2 and 3 are illustrated in figure 2.

The equilibrium oxygen pressure, pO<sub>2</sub>, over MnO + MnSO<sub>4</sub> is determined from the potential measurements for cell reaction 2, and may be expressed as

$$\text{O}_2^*(\text{g, 0.0111 atm}) = \text{O}_2(\text{g, over MnO + MnSO}_4). \quad (7)$$

The corresponding Gibbs energy change, ΔG, for reaction 7 is

$$\Delta G(\text{reaction 7}) = -nFE = RT \ln p\text{O}_2 - RT \ln p\text{O}_2^*, \quad (8)$$

where n is 4, F is the Faraday constant, E is the emf from equation 4, and pO<sub>2</sub><sup>\*</sup> is the oxygen pressure at the reference electrode. Pressures are expressed in atmospheres. Rearranging equation 8 and substituting pO<sub>2</sub><sup>\*</sup> and E from equation 4 yields

$$\log p\text{O}_2 = -\frac{35,848}{T} + 24.67 \quad (896.5-946.3 \text{ K}). \quad (9)$$

TABLE 2. - Electromotive force (E) of cells  
 A. Pt, MnSO<sub>4</sub>, MnO, SO<sub>2</sub> (g, 1 atm)//ZrO<sub>2</sub>//O<sub>2</sub> (g, 0.0111 atm), Pt  
 B. Pt, MnSO<sub>4</sub>, Mn<sub>3</sub>O<sub>4</sub>, SO<sub>2</sub> (g, 1 atm)//ZrO<sub>2</sub>//O<sub>2</sub> (g, 0.0112 atm), Pt

Measurement	Temperature, K	E, mv		Measurement	Temperature, K	E, mv	
		Measured <sup>1</sup>	Calculated <sup>2</sup>			Measured <sup>1</sup>	Calculated <sup>2</sup>
1.....	896.5	593.03±0.010	594.02	24.....	1,039.2	356.23±0.003	360.31
2.....	898.4	590.91±.005	591.51	25.....	1,040.7	357.66±.005	357.47
3.....	898.8	590.61±.005	590.98	26.....	1,040.7	355.88±.001	357.47
4.....	899.5	590.47±.005	590.06	27.....	1,041.5	355.04±.002	355.95
5.....	899.7	590.53±.020	589.80	28.....	1,043.1	354.87±.002	352.92
6.....	914.1	571.58±.025	570.78	29.....	1,043.1	355.17±.002	352.92
7.....	919.5	560.95±.015	563.64	30.....	1,060.0	319.94±.005	320.89
8.....	920.7	564.70±.005	562.06	31.....	1,065.3	313.34±.002	310.84
9.....	921.9	559.46±.010	560.47	32.....	1,085.4	272.0±.002	272.75
10.....	922.1	561.29±.015	560.21	33.....	1,085.9	271.04±.010	271.80
11.....	922.4	561.07±.015	559.81	34.....	1,087.8	267.80±.002	268.20
12.....	932.4	545.85±.005	546.60	35.....	1,088.1	269.65±.002	267.63
13.....	945.5	529.18±.015	529.30	36.....	1,104.1	236.49±.007	237.30
14.....	945.7	529.56±.010	529.04	37.....	1,128.6	189.00±.003	191.71
15.....	946.3	527.34±.045	528.24	38.....	1,129.8	189.44±.003	189.59
16.....	971.2	485.90±.003	489.20	39.....	1,131.1	193.85±.005	187.29
17.....	974.2	486.63±.003	483.52	40.....	1,146.7	155.44±.001	159.76
18.....	993.2	444.01±.002	447.50	41.....	1,172.3	113.24±.005	114.58
19.....	995.7	441.97±.002	442.76	42.....	1,210.0	46.22±.001	48.05
20.....	997.0	443.56±.002	440.30	43.....	1,211.1	48.51±.003	46.11
21.....	997.6	441.67±.004	439.16	44.....	1,213.1	47.3±.003	42.58
22.....	1,016.9	399.32±.002	402.58	45.....	1,226.8	15.03±.013	18.40
23.....	1,020.2	399.64±.001	396.33				

<sup>1</sup> Average of 2 measurements taken at 20-min intervals and corrected for cell calibration.

<sup>2</sup> Calculated from equations:

$$E = 1,778.15908 - 1.32084T \pm 1.32 \quad (896.5-946.3 \text{ K}),$$

$$E = 2,330.01553 - 1.89540T \pm 2.45 \quad (971.2-1,104.1 \text{ K}),$$

and

$$E = 2,183.52496 - 1.76486T \pm 4.03 \quad (1,128.6-1,226.8 \text{ K}).$$

NOTE.--Cell A was used for measurements for reaction 2 in temperature range 896.5 to 946.3 K (measurements 1-15); cell B was used for reaction 3 in temperature range 971.2 to 1,226.8 K (measurements 16-45).

The equilibrium oxygen pressure,  $p_{O_2}$ , over Mn<sub>3</sub>O<sub>4</sub> + MnSO<sub>4</sub> for reaction 3 is obtained by the method previously described for reaction 7. Rearranging equation 8 and substituting the value of  $p_{O_2}^0$ , the partial pressure at the reference electrode, and E for reaction 3 from equations 5 and 6 respectively, yields

$$\log p_{O_2} = -\frac{46,973}{T} + 36.26 \quad (971.2-1,104.1 \text{ K}), \quad (10)$$

and

$$\log p_{O_2} = -\frac{44,020}{T} + 33.63 \quad (1,128.6-1,226.8 \text{ K}). \quad (11)$$

Figure 3 illustrates the thermodynamic stability of that portion of the Mn-S-O system where MnO coexists with MnSO<sub>4</sub> in the temperature range 896.5 to 946.3 K and Mn<sub>3</sub>O<sub>4</sub> coexists with MnSO<sub>4</sub> in the temperature range 971.2 to 1,226.8 K. An invariant

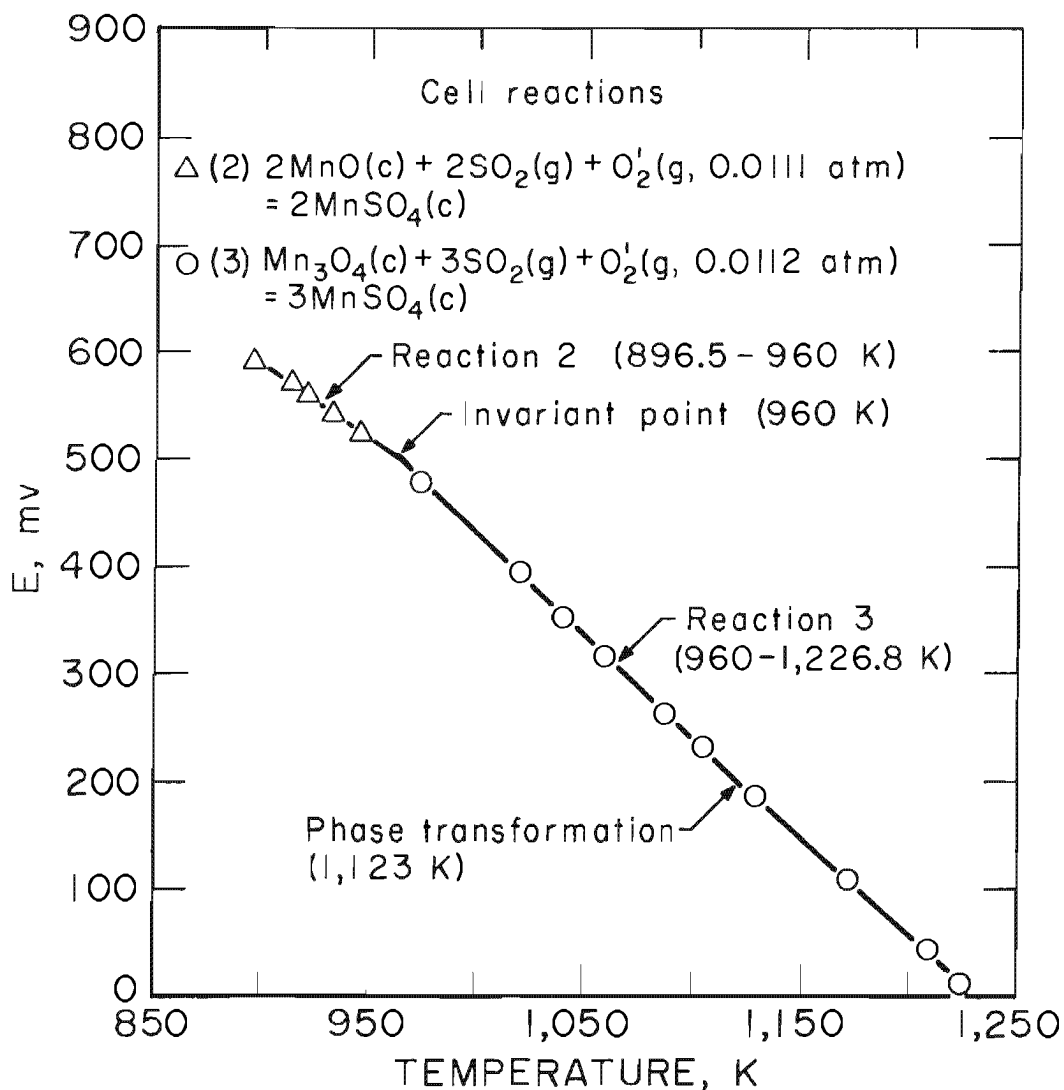
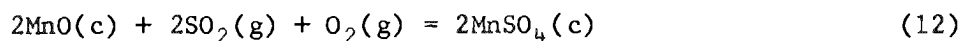
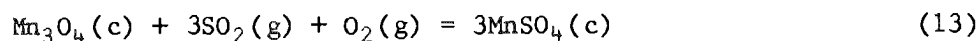


FIGURE 2. - Electromotive force (E) versus temperature for  $\text{MnSO}_4$  reactions.

point was determined at 960 K for the Mn-S-O system, and a transition of  $\text{MnSO}_4$  was detected at 1,123 K. Reaction 7 and equation 8 are independent relationships that are applicable to any equilibrium involving oxygen. These values of  $p_{\text{O}_2}$  at the reaction site are the key for computing the standard Gibbs energy changes for the reactions



and



from the relationships

$$\Delta G^\circ(\text{reaction 12}) = -RT \ln K_{12} = RT \ln p_{\text{O}_2} + 2RT \ln p_{\text{SO}_2} \quad (14)$$

and

$$\Delta G^\circ(\text{reaction 13}) = -RT \ln K_{13} = RT \ln p_{\text{O}_2} + 3RT \ln p_{\text{SO}_2}, \quad (15)$$

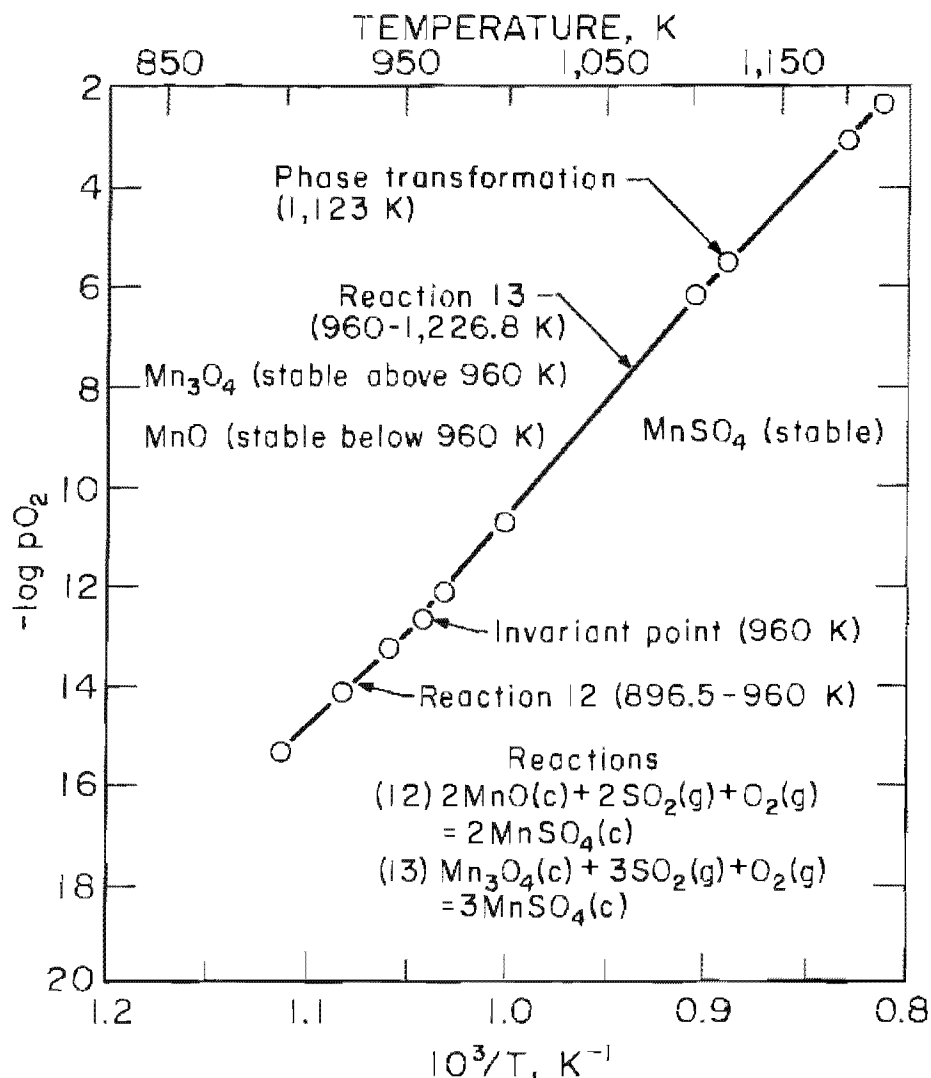
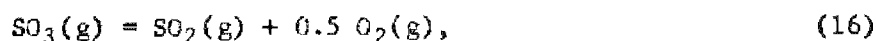


FIGURE 3. - Equilibrium diagram for  $MnO$ - $MnSO_4$ - $SO_2$ - $O_2$  and  $Mn_3O_4$ - $MnSO_4$ - $SO_2$ - $O_2$  systems.

where  $K_{12}$  and  $K_{13}$  are the equilibrium constants,  $pO_2$  is the equilibrium oxygen pressure,  $pSO_2$  is the equilibrium  $SO_2$  pressure for reactions 12 and 13, respectively, and the condensed phases are assumed to have unit activity. The equilibrium oxygen pressure is obtained from equation 9 for reaction 12 and from equation 10 or 11 for reaction 13. Resolution of the partial pressures of  $SO_2$  at the reaction site for reactions 12 and 13 involves evaluation of the following equilibrium reaction and relationships:



$$K_{p,16} = \frac{pSO_2(pO_2)^{0.5}}{pSO_3}, \quad (17)$$

and

$$P_{\text{total}} = p\text{SO}_3 + p\text{SO}_2 + p\text{O}_2, \quad (18)$$

where  $P_{\text{total}}$  is the total pressure and  $p\text{SO}_3$ ,  $p\text{SO}_2$ , and  $p\text{O}_2$  are the partial pressures of the gaseous components in atmospheres. The  $\text{SO}_2$  pressure at the interface of  $\text{MnO-MnSO}_4$  or  $\text{Mn}_3\text{O}_4\text{-MnSO}_4$  electrodes and the electrolyte was calculated by combining equations 17 and 18 to yield

$$p\text{SO}_2 = \frac{P_{\text{total}} - p\text{O}_2}{1 + (p\text{O}_2)^{0.5}/K_{p,16}}, \quad (19)$$

where  $K_{p,16}$  is the equilibrium constant for reaction 16 (equation 17), based on auxiliary data from the literature (15).

The average total pressure of the system is 0.99307 atm for the  $\text{MnO-MnSO}_4\text{-SO}_2\text{-O}_2$  equilibrium and 0.99917 atm for the  $\text{Mn}_3\text{O}_4\text{-MnSO}_4\text{-SO}_2\text{-O}_2$  measurements. Calculations show that  $p\text{SO}_2$  is 0.99307 atm in the temperature range 896.5 to 946.3 K. For the latter system,  $p\text{SO}_2$  is 0.99917 atm at 971.2 K, 0.99873 atm at 1,104.1 K, 0.99817 atm at 1,128.6, and 0.97802 atm at 1,226.8 K. Consequently, in the temperature range of this investigation, the standard Gibbs energies for reactions 12 and 13, as given by equations 14 and 15, are not appreciably affected by the slight variation of  $p\text{SO}_2$  from standard conditions.

Results of these calculations and those of previous investigators are presented in tables 3 and 4. As noted in table 3, the results from this investigation for reaction 12 are more negative than those derived from calorimetric data (14). Considerable disagreement is also noted in table 4 between the results of this investigation and those based on calorimetric measurements (11, 14) for reaction 13. Discrepancies in the data from the various investigations for reaction 13 are illustrated in figure 4.

TABLE 3. - Standard Gibbs energy change ( $-\Delta G^\circ$ ) for  $2\text{MnO}(c) + 2\text{SO}_2(g) + \text{O}_2(g) = 2\text{MnSO}_4(c)$  (kilocalories per mole  $\text{O}_2$ )

Temperature, K	Mah (calorimetry)	This investigation
896.5	57.320	62.840
900.0	56.858	62.444
946.3	50.742	57.219

TABLE 4. - Standard Gibbs energy change ( $-\Delta G^\circ$ ) for  $\text{Mn}_3\text{O}_4(c) + 3\text{SO}_2(g) + \text{O}_2(g) = 3\text{MnSO}_4(c)$  (kilocalories per mole  $\text{O}_2$ )

Temperature, K	Mah (14)	Kellogg (11)	Ingraham (7)	Turkdogan, Olsson, and Vinters (25)	Skeaff and Espelund (20)	This investigation
971.2	46.795	46.504	ND	ND	ND	53.799
1,000	41.850	41.700	ND	ND	48.930	49.022
1,100	25.350	25.138	31.497	34.637	32.628	32.434
1,123	ND	ND	28.633	31.163	28.878	28.623
1,200	ND	20.430	19.048	19.532	18.372	16.894

ND Not determined.

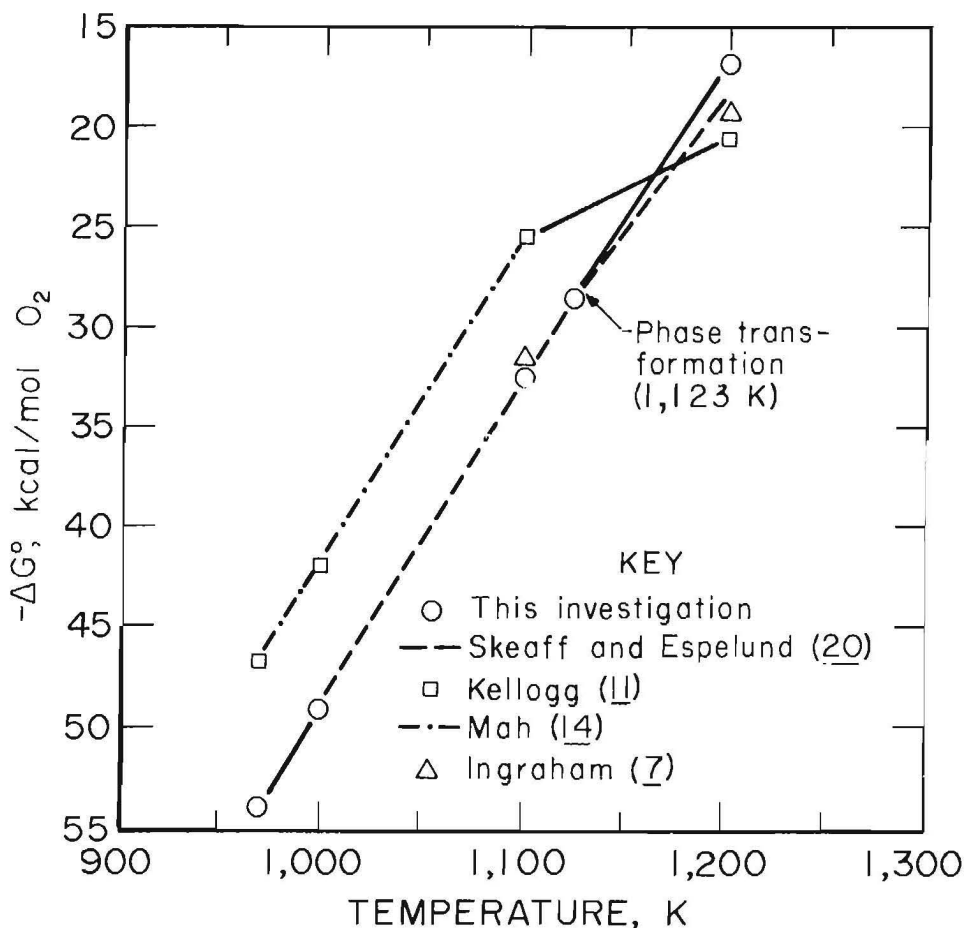
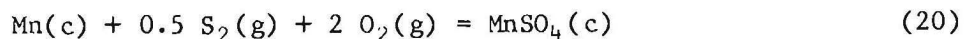


FIGURE 4. - Standard Gibbs energy change for  $\text{Mn}_3\text{O}_4(\text{c}) + 3\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) = 3\text{MnSO}_4(\text{c})$ .

X-ray diffraction analyses of electrode products are given in table 5. The results showed no major change in lattice parameters between the reagents and the components in the equilibrated electrode mixtures. The lattice parameter of a solid solution generally changes with the composition up to the saturation limit and then remains constant beyond that point. Further evidence concerning the limited solubility of sulfur in manganese oxides shows that sulfur solubility, as sulfate ions, increases from 0.055 wt pct at 1,133 K to 0.11 wt pct at 1,373 K (25). Consequently, the assumption of unit activity for the condensed phases for reactions 2 and 3 does not introduce any appreciable error in the standard Gibbs energy of formation of  $\text{MnSO}_4$  in the temperature range of this investigation.

The standard Gibbs energy of formation of  $\text{MnSO}_4$  for the reaction



was derived from the relationships

$$\Delta G^\circ(\text{reaction 12}) = 2\Delta G_f^\circ(\text{MnSO}_4) - 2\Delta G_f^\circ(\text{MnO}) - 2\Delta G_f^\circ(\text{SO}_2) \quad (21)$$



TABLE 5. - X-ray diffraction analyses of samples for  $\text{MnSO}_4$  cell

Sample	Crystal structure	Parametric measurements, $\text{\AA}$ <sup>1</sup>			Card <sup>2</sup>
		a.	b.	c.	
Reagents:					
$\text{MnO}$ .....	Cubic.....	4.445	NAp	NAp	7-230
$\text{Mn}_3\text{O}_4$ .....	Tetragonal.....	5.7621	NAp	9.4696	24-734
$\text{MnSO}_4$ .....	Orthorhombic.....	5.267	8.046	6.848	11-88
Electrode mixtures:					
$\text{MnO}^3$ .....	Cubic.....	$4.441 \pm 0.02$	NAp	NAp	7-230
$\text{MnSO}_4^3$ .....	Orthorhombic.....	$5.26 \pm .01$	$8.04 \pm 0.01$	$6.85 \pm 0.01$	11-88
$\text{Mn}_3\text{O}_4^4$ .....	Tetragonal.....	$5.76 \pm .01$	NAp	$9.46 \pm .02$	24-734
$\text{MnSO}_4^4$ .....	Orthorhombic.....	$5.26 \pm .01$	$8.04 \pm .01$	$6.86 \pm .01$	11-88

NAp Not applicable.

<sup>1</sup>Parametric measurements for reagents were obtained from the literature.

<sup>2</sup>Numbers refer to data file cards of Joint Committee of Powder Diffraction Standards, International Centre of Diffraction Data, Swarthmore, Pa.

<sup>3</sup>Mixture for  $\text{MnO}$  -  $\text{MnSO}_4$  electrode.

<sup>4</sup>Mixture for  $\text{Mn}_3\text{O}_4$  -  $\text{MnSO}_4$  electrode.

NOTE.--X-ray diffraction analyses were performed by R. A. McCune, a research chemist for the analytical laboratory at the Albany Research Center, Bureau of Mines, Albany, OR.

$$\text{and } \Delta G^\circ(\text{reaction 13}) = 3\Delta G_f^\circ(\text{MnSO}_4) - \Delta G_f^\circ(\text{Mn}_3\text{O}_4) - 3\Delta G_f^\circ(\text{SO}_2). \quad (22)$$

In equation 21, the standard Gibbs energies of formation of  $\text{MnO}$  (2),  $\text{SO}_2$  (15), and the Gibbs energy of reaction 12 from this investigation, as given in table 3, may be expressed as follows:

$$\Delta G_f^\circ(\text{MnO}) = -92.050 + 17.50 \times 10^{-3}T \pm 0.150 \text{ kcal/mol } (900-1,000 \text{ K}), \quad (23)$$

$$\Delta G_f^\circ(\text{SO}_2) = -86.545 + 17.47 \times 10^{-3}T \pm 0.050 \text{ kcal/mol } (900-1,200 \text{ K}), \quad (24)$$

$$\text{and } \Delta G^\circ(\text{reaction 12}) = -164.027 + 112.87 \times 10^{-3}T \pm 0.122 \text{ kcal } (896.5-946.3 \text{ K}). \quad (25)$$

Rearranging equation 21 and substituting the proper values for the standard Gibbs energy of reaction 12, as given by equation 25,  $\Delta G_f^\circ$  of  $\text{MnO}$  (2) from equation 23, and  $\Delta G_f^\circ$  of  $\text{SO}_2$  (15) from equation 24 yields

$$\Delta G_f^\circ(\text{MnSO}_4) = -260.609 + 91.41 \times 10^{-3}T \pm 0.169 \text{ kcal/mol } (896.5-946.3 \text{ K}). \quad (26)$$

In equation 22, the standard Gibbs energy of formation of  $\text{Mn}_3\text{O}_4$  (19) and the standard Gibbs energy of reaction 13 from this investigation, as given in table 4, may be expressed as

$$\Delta G_f^\circ(\text{Mn}_3\text{O}_4) = -329.326 + 79.46 \times 10^{-3}T \pm 0.453 \text{ kcal/mol } (746.9-1,208.6 \text{ K}), \quad (27)$$

$$\Delta G^\circ(\text{reaction 13}) = -214.913 + 165.89 \times 10^{-3}T \pm 0.226 \text{ kcal } (971.2-1,123 \text{ K}), \quad (28)$$

$$\text{and } \Delta G^\circ(\text{reaction 13}) = -199.690 + 152.33 \times 10^{-3}T \pm 0.372 \text{ kcal } (1,123-1,226.8 \text{ K}). \quad (29)$$

Rearranging equation 22 and substituting the values of  $\Delta G_f^\circ$  of  $Mn_3O_4$  from equation 27,  $\Delta G^\circ$  of reaction 13 from equation 28 or 29, and  $\Delta G_f^\circ$  of  $SO_2$  from equation 24 yields the standard Gibbs energy of formation of  $MnSO_4$ , which may be expressed by the linear equations

$$\Delta G_f^\circ(MnSO_4) = -267.958 + 99.25 \times 10^{-3}T \pm 0.176 \text{ kcal/mol}; (971.2-1,123 \text{ K}) \quad (30)$$

and

$$\Delta G_f^\circ(MnSO_4) = -262.884 + 94.73 \times 10^{-3}T \pm 0.202 \text{ kcal/mol} \quad (1,123-1,226.8 \text{ K}). \quad (31)$$

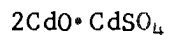
A phase change in  $MnSO_4$  occurs at 1,123 K. An enthalpy of approximately  $15.223 \pm 0.226$  kcal for reaction 13 or 5.074 kcal/mol  $MnSO_4$  is associated with this transition. This value compares with  $10.850 \pm 1.220$  kcal/mol, which has been reported in the literature (20) and was also obtained from emf measurements.

A third-law analysis using the Gibbs energy of formation of  $MnSO_4$  from equation 30, combined with entropy and enthalpy data for Mn (6),  $O_2$  (15), rhombic sulfur (9-10), and  $MnSO_4$  (9-10) yields a standard enthalpy of formation of  $MnSO_4$ ,

$$\Delta H_f^\circ_{298} = -257.674 \pm 0.20 \text{ kcal/mol}, \quad (32)$$

where the standard states are pure crystalline Mn and  $MnSO_4$ , gaseous  $O_2$  at unit fugacity, and rhombic sulfur. The calculated value  $-257.674 \pm 0.20$  kcal/mol compares with  $-254.18 \pm 0.250$  kcal/mol, which was obtained by solution calorimetry (21) and has been reported in three compilations (11, 14, 26). Calorimetric data were presumably from measurements of stoichiometric  $MnSO_4$  and should provide excellent standard-state data. Unfortunately, the standard-state properties may be quite different from the actual properties of  $MnSO_4$  that is in equilibrium with  $MnO$  or  $Mn_3O_4$ .

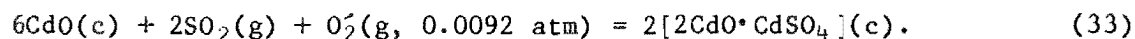
These discrepancies between the hypothetical standard-state and actual equilibrium properties are probably related to the defect structure of  $MnO$  crystal that was discussed in a recent publication (19). Prediction of chemical behavior of a system by means of thermodynamic data for the hypothetical standard-state composition can be seriously in error at high temperatures if the homogeneous range of each phase is not taken into consideration. Calculation of the Gibbs energy change in going from the standard composition to the actual equilibrium composition corresponds to knowing the activity coefficient as a function of composition within the homogeneous range. Since the equilibrium behavior can vary considerably with composition, the degree of nonstoichiometry must be specified to fix the chemical behavior of the compound. Consequently, any calculations of the dissociation temperatures, pressures, and Gibbs energies for the Mn-S-O system that are based on calorimetric data for  $MnSO_4$  and  $Mn_3O_4$  should be regarded as crude estimates for the actual equilibrium conditions at high temperatures. Standard Gibbs energy changes for reaction 13, which are derived from actual oxygen pressures (equation 10 or 11), are considered to be a more realistic characterization of the actual equilibrium conditions for defining the coexistence of  $Mn_3O_4$  and  $MnSO_4$  than are the calorimetric data.



The equilibrium oxygen pressure and corresponding Gibbs energy change for the  $CdO-2CdO \cdot CdSO_4-SO_2-O_2$  system were determined by measuring the open-circuit potentials for the cell

Pt,  $2\text{CdO} \cdot \text{CdSO}_4$ , CdO,  $\text{SO}_2(\text{g}, 1 \text{ atm}) // \text{ZrO}_2 // \text{O}_2^*(\text{g}, 0.00922 \text{ atm})$ , Pt,

where the partial pressure of  $\text{O}_2^*$  at the reference electrode is 0.00922 atm and  $\text{SO}_2$  is at 1 atm. The overall cell reaction is



Potential measurements from four cells that were used for the  $2\text{CdO} \cdot \text{CdSO}_4$  determination are given in table 6. These results may be expressed as a function of temperature by the linear equation and standard error of estimate

$$E = 1,945.99 - 1.47048T \pm 2.12 \quad (1,036.8-1,208.2 \text{ K}), \quad (34)$$

where E is in millivolts. Potential measurements and their corresponding smooth values, derived from equation 34, are given in columns 3, 4, 7, and 8 of table 6. Representative emf-versus-temperature data are illustrated in figure 5.

The equilibrium oxygen pressure,  $p\text{O}_2$ , and the corresponding Gibbs energy change for reaction 33 are obtained by the method previously described for reaction 7. Rearranging equation 8 and substituting the value of  $p\text{O}_2^*$ , the partial pressure of

TABLE 6. - Electromotive force (E) of cell  
Pt,  $2\text{CdO} \cdot \text{CdSO}_4$ , CdO,  $\text{SO}_2(\text{g}, 1 \text{ atm}) // \text{ZrO}_2 // \text{O}_2^*(\text{g}, 0.00922 \text{ atm})$ , Pt

Measurement	Temperature, K	E, mv		Measurement	Temperature, K	E, mv	
		Measured <sup>1</sup>	Calculated <sup>2</sup>			Measured <sup>1</sup>	Calculated <sup>2</sup>
1.....	1,036.8	419.11	421.40	21.....	1,145.6	265.15	261.41
2.....	1,037.1	419.31	420.96	22.....	1,146.3	262.94	260.38
3.....	1,037.6	420.21	420.22	23.....	1,147.1	258.35	259.20
4.....	1,059.2	386.58	388.46	24.....	1,158.2	236.48	242.88
5.....	1,060.1	387.08	387.13	25.....	1,166.6	232.01	230.53
6.....	1,060.2	388.28	386.99	26.....	1,166.8	227.91	230.23
7.....	1,060.6	387.38	386.40	27.....	1,167.2	226.12	229.65
8.....	1,081.1	354.75	356.25	28.....	1,169.1	226.91	226.85
9.....	1,082.0	355.05	354.93	29.....	1,179.5	208.44	211.56
10.....	1,082.3	356.55	354.49	30.....	1,187.0	198.47	200.53
11.....	1,082.3	355.85	354.49	31.....	1,187.0	202.57	200.53
12.....	1,103.5	321.81	323.32	32.....	1,187.0	200.87	200.53
13.....	1,103.9	324.51	322.73	33.....	1,187.6	198.41	199.65
14.....	1,104.0	323.42	322.58	34.....	1,187.9	198.67	199.21
15.....	1,122.4	296.30	295.52	35.....	1,188.6	197.45	198.18
16.....	1,125.2	294.38	291.41	36.....	1,189.3	197.94	197.15
17.....	1,125.3	292.98	291.26	37.....	1,206.3	172.03	172.15
18.....	1,125.4	293.38	291.11	38.....	1,207.0	174.43	171.12
19.....	1,144.4	260.54	263.17	39.....	1,207.9	169.63	169.80
20.....	1,145.4	262.54	261.70	40.....	1,208.2	170.63	169.36

<sup>1</sup> Average of 2 measurements ( $\pm 0.05$  mv) taken at 15-min intervals and corrected for cell calibration.

<sup>2</sup> Calculated from linear equation:

$$E = 1,945.99 - 1.47048T \pm 2.12.$$

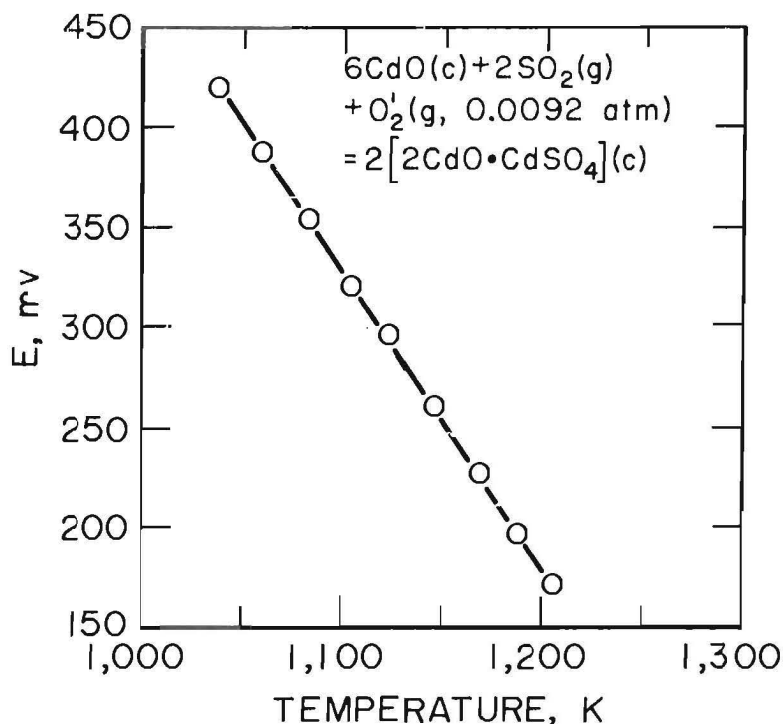
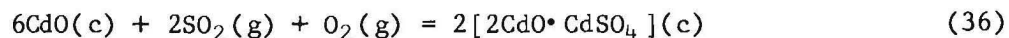


FIGURE 5. - Electromotive force (E) versus temperature for  $2\text{CdO} \cdot \text{CdSO}_4$  reaction.

$\text{O}_2$  at the reference electrode, and E from equation 34 yields

$$\log p\text{O}_2 = -\frac{39,231}{T} + 27.61. \quad (35)$$

Figure 6 illustrates the thermodynamic stability of the Cd-S-O system where CdO and  $2\text{CdO} \cdot \text{CdSO}_4$  coexist in the temperature range 1,036.8 to 1,208.2 K. These values of  $p\text{O}_2$  are the key for computing the standard Gibbs energy change for the reaction



from the relationship

$$\Delta G^\circ(\text{reaction 36}) = -RT \ln K_{36} = RT \ln p\text{O}_2 + 2RT \ln p\text{SO}_2, \quad (37)$$

where  $K_{36}$ ,  $p\text{O}_2$ , and  $p\text{SO}_2$  are the equilibrium constant and the equilibrium pressures of  $\text{O}_2$  and  $\text{SO}_2$  for reaction 36. The equilibrium oxygen pressure is from equation 35, and  $p\text{SO}_2$  is derived by the method previously described in equations 16 through 19. The condensed phases in reaction 36 are assumed to have unit activity.

The average total pressure of the system for the  $2\text{CdO} \cdot \text{CdSO}_4$  measurements is 0.99947 atm. Calculations show that  $p\text{SO}_2$  ranges from 0.99946 atm at 1,036.8 K to 0.99577 atm at 1,208.2 K. Consequently, in the temperature range of this investiga-

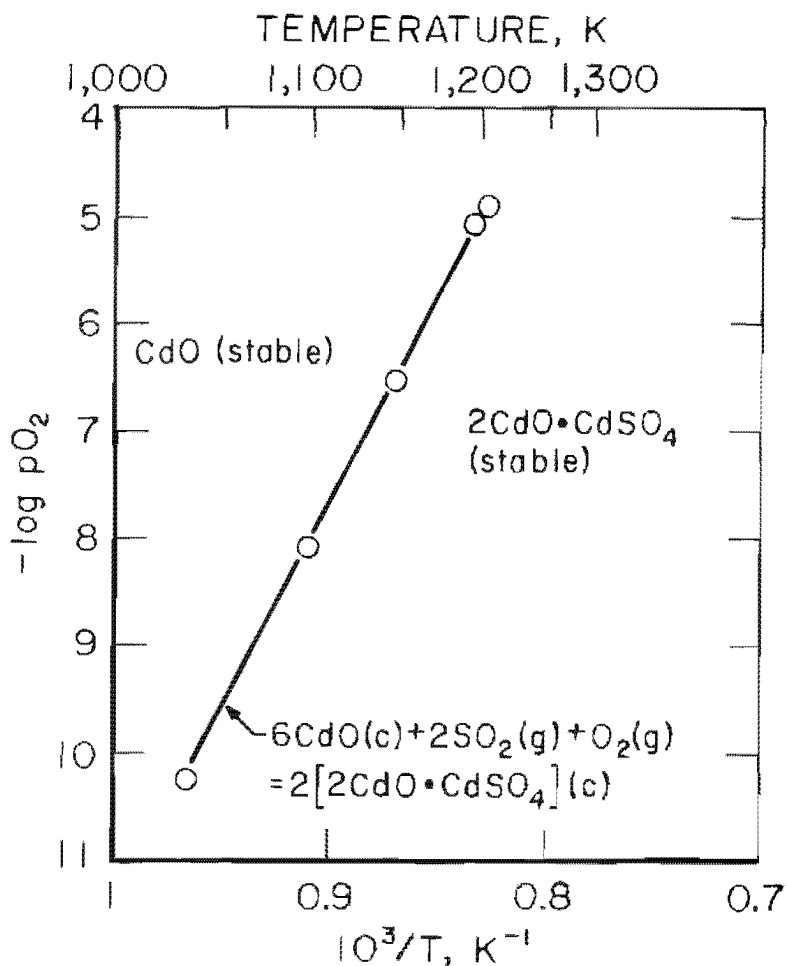


FIGURE 6. - Equilibrium diagram for CdO-2CdO·CdSO<sub>4</sub>-SO<sub>2</sub>-O<sub>2</sub> system.

tion, the standard Gibbs energy for reaction 36, as given by equation 37, is not appreciably affected by the slight variation of  $p\text{SO}_2$  from standard conditions. Results of the measurements for  $p\text{O}_2$  and the corresponding values of  $p\text{SO}_2$  and Gibbs energies for reaction 36 are given in table 7 and illustrated in figure 7.

X-ray diffraction analyses of electrode products are given in table 8.

TABLE 7. - Standard Gibbs energy change for  $6\text{CdO}(\text{c}) + 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) = 2[2\text{CdO} \cdot \text{CdSO}_4](\text{c})$

Temperature, K	$p\text{SO}_2$ , atm	$p\text{O}_2$ , atm	$-\Delta G^\circ$ , kcal/mol O <sub>2</sub>
1,036.8	0.99946	$5.9030 \times 10^{-11}$	48.528
1,100.0	.99941	$8.8117 \times 10^{-9}$	40.545
1,150	.99925	$3.1000 \times 10^{-7}$	34.251
1,200	.99873	$8.2600 \times 10^{-6}$	27.916
1,208.2	.998576	$1.3770 \times 10^{-5}$	26.880

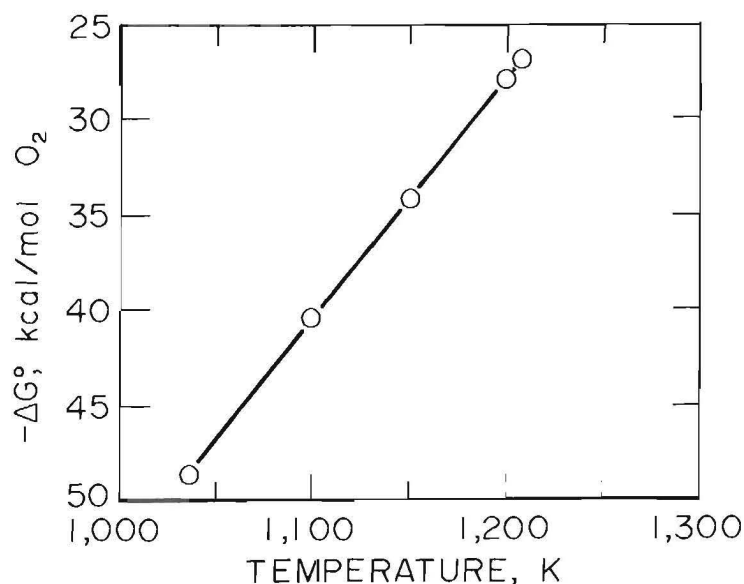


FIGURE 7. - Standard Gibbs energy change for  $6CdO(c) + 2SO_2(g) + O_2(g) = 2[2CdO \cdot CdSO_4](c)$ .

TABLE 8. - X-ray diffraction analyses for  $2CdO \cdot CdSO_4$  cell

Sample	Crystal structure	Parametric measurements, Å <sup>1</sup>			Card <sup>2</sup>
		a <sub>o</sub>	b <sub>o</sub>	c <sub>o</sub>	
Reagents:					
CdO.....	Cubic.....	4.6953	NAp	NAp	5-640
2CdO·CdSO <sub>4</sub> .....	Orthorhombic.....	6.97	23.34	6.85	26-382
Electrode mixture:					
CdO.....	Cubic.....	4.695±0.001	NAp	NAp	5-640
2CdO·CdSO <sub>4</sub> .....	Orthorhombic.....	6.95 ± .01	23.29±0.03	6.84±0.01	26-382

NAp Not applicable.

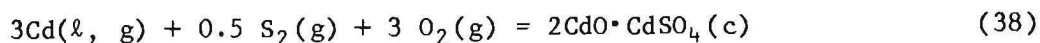
<sup>1</sup>Parametric measurements for reagents were obtained from the literature.

<sup>2</sup>Numbers refer to data file cards of Joint Committee of Powder Diffraction Standards, International Centre of Diffraction Data, Swarthmore, Pa.

NOTE.--X-ray diffraction analyses were performed by R. A. McCune, a research chemist for the analytical laboratory at the Albany Research Center, Bureau of Mines, Albany, OR.

The results showed no major change in lattice parameters between the reagents and the components in the equilibrated electrode mixture. Consequently, intersolubility of the condensed components in the  $CdO + 2CdO \cdot CdSO_4$  electrode mixture is negligible and the assumption of unit activity for the condensed phases in reaction 36 does not introduce any appreciable error in the standard Gibbs energy of formation of  $2CdO \cdot CdSO_4$ .

The standard Gibbs energy of formation of  $2CdO \cdot CdSO_4$  for the reaction



was derived from the relationship

$$\Delta G^\circ(\text{reaction 36}) = 2\Delta G_f^\circ(2\text{CdO} \cdot \text{CdSO}_4) - 6\Delta G_f^\circ(\text{CdO}) - 2\Delta G_f^\circ(\text{SO}_2). \quad (39)$$

In equation 39, the standard Gibbs energies of formation of CdO (16), SO<sub>2</sub> (15) from equation 24, and the standard Gibbs energy of reaction 36 from this investigation, as given in table 7, may be expressed as follows:

$$\Delta G_f^\circ(\text{CdO}) = -85.659 + 47.21 \times 10^{-3}T \pm 0.200 \text{ kcal/mol} \quad (1,000-1,200 \text{ K}), \quad (40)$$

$$\begin{aligned} \Delta G^\circ(\text{reaction 36}) = & -179.475 + 126.30 \times 10^{-3}T \\ & \pm 0.196 \text{ kcal} \quad (1,036.8-1,208.2 \text{ K}). \end{aligned} \quad (41)$$

Rearranging equation 39 and substituting the standard Gibbs energy of reaction 36 from equation 41,  $\Delta G_f^\circ$  of SO<sub>2</sub> from equation 24, and  $\Delta G_f^\circ$  of CdO from equation 40, yields a standard Gibbs energy of formation of 2CdO·CdSO<sub>4</sub> for reaction 38, which may be expressed as

$$\begin{aligned} \Delta G_f^\circ(2\text{CdO} \cdot \text{CdSO}_4) = & -433.260 + 222.25 \times 10^{-3}T \\ & \pm 0.610 \text{ kcal/mol} \quad (1,036.8-1,208.2 \text{ K}). \end{aligned} \quad (42)$$

No experimental entropy and enthalpy data are available for 2CdO·CdSO<sub>4</sub>; consequently, a third-law analysis from experimental data cannot be made. Assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  remain fairly constant in the temperature range 1,036.8 to 1,208.2 K, the enthalpy and entropy for reaction 38 at 1,122.5 K, according to the first and second constants in equation 42, are

$$\Delta H_f^\circ = -433.260 \pm 0.610 \text{ kcal/mol} \quad (43)$$

$$\text{and} \quad \Delta S_f^\circ = -222.25 \text{ cal/mol} \cdot \text{K}. \quad (44)$$

The standard states at 1,122.5 K are pure gaseous cadmium at unit fugacity, crystalline 2CdO·CdSO<sub>4</sub>, and gaseous S<sub>2</sub> and O<sub>2</sub> at unit fugacity.

#### SUMMARY AND CONCLUSIONS

Equilibrium oxygen pressures for the MnO-MnSO<sub>4</sub>-SO<sub>2</sub>-O<sub>2</sub>, Mn<sub>3</sub>O<sub>4</sub>-MnSO<sub>4</sub>-SO<sub>2</sub>-O<sub>2</sub>, and CdO-2CdO·CdSO<sub>4</sub>-SO<sub>2</sub>-O<sub>2</sub> systems were measured by a high-temperature emf method using stabilized ZrO<sub>2</sub> as the solid electrolyte. The emf measurements yielded standard Gibbs energies of formation of MnSO<sub>4</sub> and 2CdO·CdSO<sub>4</sub> from their oxides. The data for MnSO<sub>4</sub> were compared with previously reported measurements, and discrepancies were discussed. No previous Gibbs energies of formation have been reported for 2CdO·CdSO<sub>4</sub> to permit direct comparison. Standard thermodynamic properties of MnSO<sub>4</sub> were derived by combining results from this investigation with auxiliary data from the literature.

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